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ance Notes on Codes and Abbreviations" appearing at the begin-
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(54) Title: POLYETHYLENE COMPOSITION FOR PRODUCING L-RING DRUMS

(57) Abstract: The invention relates to a polyethylene composition with multimodal molecular mass distribution, which is particularly suitable for the blow molding of L-ring drums having a volume in the range of from 50 to 250 dm³ (I). The composition has a density in the range of from 0.950 to 0.956 g/cm³ at 23 °C and a MFR_{1g/21.6} in the range from 1.5 to 3.5 dg/min. It comprises from 35 to 45 % by weight of a low-molecular-mass ethylene homopolymer A, from 34 to 44 % by weight of a high-molecular-mass copolymer B made from ethylene and from another 1-olefin having from 4 to 8 carbon atoms, and from 18 to 26 % by weight of an ultrahigh-molecular-mass ethylene copolymer C.



WO 2004/058877 A1

Title: Polyethylene composition for producing L-ring drums

The present invention relates to a polyethylene composition with multimodal
5 molecular mass distribution, which is particularly suitable for the blow molding
of L-ring drums with a capacity (volume) in the range of from 50 to 250 dm³ (l),
and to a process for preparing this composition in the presence of a catalytic
system composed of a Ziegler catalyst and a cocatalyst like triethylaluminum,
triisobutylaluminum, alkylaluminumchlorides and alkylaluminumhydrides, by
10 way of a multistage process composed of successive slurry polymerizations.
The invention further relates to the L-ring containers produced from the
composition by blow molding.

Polyethylene is widely used for producing moldings of all types requiring a
15 material with particularly high mechanical strength, high corrosion resistance,
and absolutely reliable long-term stability. Another particular advantage of
polyethylene is that it also has good chemical resistance and is intrinsically a
light-weight material.

20 EP-A-603,935 has previously described a blow molding composition based on
polyethylene and having a bimodal molecular mass distribution, and suitable for
the production of moldings with good mechanical properties.

US-A 5,338,589 describes a material with even wider molecular mass
25 distribution, prepared using a high-mileage catalyst known from WO 91/18934,
in which the magnesium alcoholate is used in the form of a gel-like suspension.
Surprisingly, it has been found that the use of this material in moldings permits
simultaneous improvement in properties which are usually contrary correlated
in semicrystalline thermoplastics, these being stiffness on the one hand and
30 stress-crack resistance and toughness on the other hand.

However, the known bimodal products, in particular, have relatively low melt strength during processing. This means that the extruded parison frequently break in the molten state, making the extrusion process unacceptably sensitive to processing. In addition, especially when thick-walled containers are being produced, the wall thickness is found to be non-uniform, due to flow of the polymer melt from upper regions into lower regions of the molding before solidification.

It is an objective of the present invention, therefore, to develop a polyethylene composition for blow molding which shows a further improvement over all of the known materials in processing by blow molding to produce L-ring drums. In particular, the high melt strength of the composition should permit to run an extrusion process without parison disruption over a long time period, whereas the precisely adjusted swell ratio of the composition should permit optimization of wall-thickness control. In addition, the molding composition has to be sufficiently tough for forklift and truck transportation of filled L-ring drums.

We have surprisingly found that this objective is achieved by way of a composition as mentioned at the outset, the characterizing features of which are that it comprises from 35 to 45 % by weight of a low-molecular-mass ethylene homopolymer A, from 34 to 44 % by weight of a high-molecular-mass copolymer B made from ethylene and from another 1-olefin having from 4 to 8 carbon atoms, and from 18 to 26 % by weight of an ultrahigh-molecular-mass ethylene copolymer C, wherein all of the percentage data are based on the total weight of the molding composition.

The invention also relates to a process for preparing this composition in a cascaded slurry polymerization and to a process for producing, from this composition, L-ring drums with a capacity or volume in the range of from 50 to 250 dm³ (l) and with quite excellent mechanical strength properties.

The polyethylene composition of the invention has a density in the range of from 0.950 to 0.956 g/cm³ at 23 °C, and a broad trimodal molecular mass distribution. The high-molecular-mass copolymer B contains only small proportions of other 1-olefin monomer units having from 4 to 8 carbon atoms,
5 namely less than 0.1 % by weight. Examples of these comonomers are 1-butene, 1-pentene, 1-hexene, 1-octene, or 4-methyl-1-pentene. The ultrahigh-molecular-mass ethylene homo- or copolymer C also contains an amount in the range from 0.1 to 0.6 % by weight of one or more of the above-mentioned co-monomers.

10

The polymer composition of the invention also has a melt flow index ISO 1133 in the range of from 1.5 to 3.5 dg/min expressed in terms of MFR_{190/21.6}, and a viscosity number VN_{tot} in the range of from 500 to 600 cm³/g measured according to ISO/R 1191 in decalin at 135 °C.

15

The trimodality is a measure of the position of the centers of gravity of the three individual molecular mass distributions, and can be described with the aid of the viscosity number VN to ISO/R 1191 of the polymers formed in the successive polymerization stages. The relevant band widths for the polymers
20 formed in each of the stages of the reaction are therefore as follows:

The viscosity number VN₁ measured on the polymer after the first polymerization stage is identical with the viscosity number VN_A of the low-molecular-mass polyethylene A and according to the invention is in the range of
25 from 160 to 220 cm³/g.

The viscosity number VN₂ measured on the polymer after the second polymerization stage is not equal to VN_B of the high-molecular-mass polyethylene B formed in the second polymerization stage, which can only be
30 determined by calculation, but rather represents the viscosity number of the

mixture of polymer A and polymer B. According to the invention, VN_2 is in the range of from 230 to 320 cm^3/g .

5 The viscosity number VN_3 measured on the polymer after the third polymerization stage is not equal to VN_c of the ultra-high-molecular-mass copolymer C formed in the third polymerization stage, which can only be determined by calculation, but rather represents the viscosity number of the mixture of polymer A, polymer B, and polymer C. According to the invention, VN_3 is in the range of from 500 to 600 cm^3/g .

10

The polyethylene is obtained by polymerizing the monomers in slurry in a temperature range of from 60 to 90 °C, at a pressure in the range of from 0,15 to 1 MPa, and in the presence of a high-mileage Ziegler catalyst composed of a transition metal compound and of triethylaluminum as organoaluminum
15 compound. The polymerization is conducted in three stages, i.e. in three stages arranged in series, each molecular mass being regulated with the aid of a hydrogen feed.

The polyethylene composition of the invention may comprise other additives
20 alongside the polyethylene. Examples of these additives are heat stabilizers, antioxidants, UV absorbers, light stabilizers, metal deactivators, compounds which destroy peroxide, and basic co-stabilizers in amounts of from 0 to 10 % by weight, preferably from 0 to 5 % by weight, and also fillers, reinforcing agents, plasticizers, lubricants, emulsifiers, pigments, optical brighteners, flame
25 retardants, antistats, blowing agents, or a combination of these, in total amounts of from 0 to 50 % by weight, based on the total weight of the mixture.

The composition of the invention is particularly suitable for the blow molding process to produce L-ring drums, by first plastifying the polyethylene
30 composition in an extruder in a temperature range of from 200 to 250 °C and

then extruding it through a die into a mold, where it is blown up and then cooled and solidified.

5 The composition of the invention gives particularly good processing behavior in the blow molding process to give L-ring drums because it has a swell ratio in the range of from 180 to 220 %, and the L-ring drums produced therewith have particularly high mechanical strength because the composition of the invention has a notched impact strength (ISO) in the range of from 60 to 90 kJ/m². The stress-crack resistance (FNCT) is in the range of from 15 to 25 h.

10

The notched impact strength_{ISO} is measured according to ISO 179-1/1eA / DIN 53453 at 23 °C. The size of the specimen is 10 x 4 x 80 mm, and a V notch is inserted using an angle of 45°, with a depth of 2 mm and with a notch base radius of 0.25 mm.

15

The stress-crack resistance of the composition of the invention is determined by an internal test method and is given in h. This laboratory method is described by M. Fleißner in Kunststoffe 77 (1987), pp. 45 et seq., and corresponds to ISO/CD 16770, which has since come into force. The
20 publication shows that there is a relationship between determination of slow crack growth in the creep test on specimens with a circumferential notch and the brittle section of the long-term internal- and hydrostatic-pressure test to ISO 1167. In ethylene glycol as stress-crack-promoting medium at 80°C with a tensile stress of 3.5 MPa, the time to failure is shortened due to the shortening
25 of the stress-initiation time by the notch (1.6 mm/razorblade). The specimens are produced by sawing out three specimens of dimensions 10 x 10 x 110 mm from a pressed plaque of thickness 10 mm. These specimens are provided with a central notch, using a razorblade in a notching device specifically manufactured for the purpose (see Figure 5 in the publication). The notch depth
30 is 1.6 mm.

Working Example

Ethylene was polymerized in a continuous process in three reactors arranged in series. An amount of 5.5 mmol/h of a Ziegler catalyst prepared as specified in WO 91/18934, Example 2, and having the operative number 2.2 in the WO,
5 was fed into the first reactor together with 150 mmol/h triethylaluminum, as well as sufficient amounts of diluent (hexane), ethylene and hydrogen. The amount of ethylene (= 49.4 kg/h) and the amount of hydrogen (= 18 g/h) were adjusted so that the percentage proportion of ethylene and of hydrogen measured in the gas phase of the first reactor were from 49 % by volume and 43 % by volume,
10 respectively, and the rest was a mix of nitrogen and vaporized diluent.

The polymerization in the first reactor was carried out at 73 °C.

The slurry from the first reactor was then transferred into a second reactor, in
15 which the percentage proportion of hydrogen in the gas phase had been reduced to 20 % by volume, and an amount of 15 g/h of 1-butene was added to this reactor alongside with 46.9 kg/h of ethylene. The amount of hydrogen was reduced by way of intermediate H₂ depressurization. 72 % by volume of ethylene, 20 % by volume of hydrogen, and < 0.1% by volume of 1-butene were
20 measured in the gas phase of the second reactor, the rest being a mix of nitrogen and vaporized diluent.

The polymerization in the second reactor was carried out at 85 °C.

25 The slurry from the second reactor was transferred to the third reactor using further intermediate H₂ depressurization to adjust the amount of hydrogen to less than 0.1 % by volume in the gas phase of the third reactor.

An amount of 90 g/h of 1-butene was added to the third reactor alongside with
30 an amount of 27.2 kg/h of ethylene. A percentage proportion of 91 % by volume

of ethylene, less than 0.1 % by volume of hydrogen, and 0.22 % by volume of 1-butene was measured in the gas phase of the third reactor, the rest being a mix of nitrogen and vaporized diluent.

- 5 The polymerization in the third reactor was carried out at 76 °C.

The long-term polymerization catalyst activity required for the cascaded process described above was provided by a specifically developed Ziegler catalyst as described in the WO mentioned at the outset. A measure of the usefulness of
10 this catalyst is its extremely high hydrogen sensitivity and its uniformly high activity over a long time period of between 1 to 8 h.

The diluent is removed from the polymer slurry leaving the third reactor, and the polymer is dried and then pelletized.

15

Table 1 shown below gives the viscosity numbers and quantitative proportions w_A , w_B , and w_C of polymer A, B, and C for the polyethylene composition prepared in Example 1.

20 Table 1

Example	
density [g/cm ³]	0.953
MFR _{190/21.6} [dg/min]	2.6
w_A [% by weight]	40
w_B [% by weight]	38
w_C [% by weight]	22
VN ₁ [cm ³ /g]	210

VN ₂ [cm ³ /g]	260
VN _{tot} [cm ³ /g]	540
SR [%]	200
FNCT [h]	17.5
NIS _{ISO} [kJ/m ²]	80

The abbreviations for physical properties in Table 1 have the following meanings:

- 5 - SR (= swell ratio) in [%] measured in a high-pressure capillary rheometer at a shear rate of 1440 s⁻¹, in a 2/2 round-section die with conical inlet (angle = 15°) at 190 °C.
- FNCT = stress-crack resistance (Full Notch Creep Test) tested using the
- 10 internal test method of M. Fleißner, in [h].
- NIS_{ISO} = notched impact strength measured to ISO 179-1/1eA / DIN 53453 in [kJ/m²] at 23 °C.

15

* * * * *

We claim

5

1. A polyethylene composition with multimodal molecular mass distribution, which has a density in the range of from 0.950 to 0.956 g/cm³ at 23 °C and an MFR_{190/21.6} in the range of from 1.5 to 3.5 dg/min and which
10 comprises from 35 to 45 % by weight of a low-molecular-mass ethylene homopolymer A, from 34 to 44 % by weight of a high-molecular-mass copolymer B made from ethylene and from another 1-olefin having from 4 to 8 carbon atoms, and from 18 to 26 % by weight of an ultrahigh-molecular-mass ethylene copolymer C, wherein all of the percentage data are
15 based on the total weight of the molding composition.
2. A polyethylene molding composition as claimed in claim 1, wherein the high-molecular-mass copolymer B contains small proportions of less than 0.1 % by weight of co-monomer having from 4 to 8 carbon atoms, based
20 on the weight of copolymer B, and wherein the ultrahigh-molecular-mass ethylene copolymer C contains an amount in the range from 0.1 to 0.6 % by weight of co-monomers, based on the weight of copolymer C.
3. A polyethylene composition as claimed in claim 1 or 2, which, as a co-
25 monomer, contains 1-butene, 1-pentene, 1-hexene, 1-octene, 4-methyl-1-pentene, or mixtures of these.
4. A polyethylene composition as claimed in one or more of claims 1 to 3, which has a viscosity number VN_{tot} of from 500 to 600 cm³/g measured to
30 ISO/R 1191 in decalin at 135 °C.

5. A polyethylene composition as claimed in one or more of claims 1 to 4, which has a swell ratio in the range from 180 to 220 %, and a notched impact strength (ISO) in the range from 60 to 90 kJ/m², and a stress-crack resistance (FNCT) in the range from 15 to 25 h.
- 5 6. A process for producing a polyethylene composition as claimed in one or more of claims 1 to 5, in which the monomers are polymerized in slurry in a temperature range of from 60 to 90 °C at a pressure in the range of from 0.15 to 1.0 MPa, and in the presence of a high-mileage Ziegler catalyst
- 10 composed of a transition metal compound and of an organoaluminum compound, which comprises conducting polymerization in three stages, wherein the molecular mass of each polyethylene prepared in each stage is regulated with the aid of hydrogen.
- 15 7. A process as claimed in claim 6, wherein the hydrogen concentration in the first polymerization stage is adjusted so that the viscosity number VN₁ of the low-molecular-mass polyethylene A is in the range of from 160 to 220 cm³/g.
- 20 8. A process as claimed in claim 6 or 7, wherein the hydrogen concentration in the second polymerization stage is adjusted so that the viscosity number VN₂ of the mixture of polymer A and polymer B is in the range of from 230 to 320 cm³/g.
- 25 9. A process as claimed in any of claims 6 to 8, wherein the hydrogen concentration in the third polymerization stage is adjusted so that the viscosity number VN₃ of the mixture of polymer A, polymer B, and polymer C is in the range of from 500 to 600 cm³/g.
- 30 10. The use of a polyethylene composition as claimed in one or more of claims 1 to 5 for producing L-ring drums with a capacity in the range of

from 50 to 250 dm³ (l), where the polyethylene composition is first plasticized in an extruder in a temperature range of from 200 to 250 °C and is then extruded through a die into a mold, where it is blown up and then cooled and solidified.

* * * * *

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/13974

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L23/04 C08F297/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 199 45 980 A (ELENAC GMBH) 29 March 2001 (2001-03-29) the whole document -----	1-10
X	US 4 536 550 A (IKEGAMI TADASHI ET AL) 20 August 1985 (1985-08-20) the whole document -----	1-10
X	US 4 336 352 A (SAKURAI HISAYA ET AL) 22 June 1982 (1982-06-22) the whole document -----	1-10
A	US 6 242 548 B1 (KASPAR HARALD ET AL) 5 June 2001 (2001-06-05) the whole document ----- -/--	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Internatl .pplication No
PCT/L J3/13974

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Internal application No

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INTERNATIONALER RECHERCHENBERICHT

Intern: : Aktenzeichen

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A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES
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Nach der Internationalen Patentklassifikation (IPK) oder nach der nationalen Klassifikation und der IPK

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Recherchiertes Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)
IPK 7 C08L C08F

Recherchierte aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

EPO-Internal, WPI Data, PAJ

C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
X	DE 199 45 980 A (ELENAC GMBH) 29. März 2001 (2001-03-29) das ganze Dokument -----	1-10
X	US 4 536 550 A (IKEGAMI TADASHI ET AL) 20. August 1985 (1985-08-20) das ganze Dokument -----	1-10
X	US 4 336 352 A (SAKURAI HISAYA ET AL) 22. Juni 1982 (1982-06-22) das ganze Dokument -----	1-10
A	US 6 242 548 B1 (KASPAR HARALD ET AL) 5. Juni 2001 (2001-06-05) das ganze Dokument ----- -/-	1-10

☒ Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen

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Absendedatum des internationalen Recherchenberichts

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Name und Postanschrift der Internationalen Recherchenbehörde

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INTERNATIONALER RECHERCHENBERICHT

Internat Aktenzeichen

PCT/EP 03/13974

C.(Fortsetzung) ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
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